CHARACTERIZATION OF CARBON IN FLY ASH BY PARTIAL OXIDATION

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INTRODUCTION

Fly ash from coal combustion is often used as a replacement for some of the Portland cement in concrete mixtures. Surfactants are added to concrete mixtures as air entraining admixtures (AEAs), primarily to stabilize an optimum amount of air in the concrete product, thus improving its workability and durability to freeze-thaw cycles[1]. This research seeks to address the nature of any interaction between the fly ash and surfactants in concrete mixtures.

Characterization of the carbon forms in fly ash is germane to understanding fly ash/AEA interactions in concrete mixtures[2]. A better understanding of the interaction between AEA and unburned carbon forms in fly ash/cement mixtures may lead to improved methodology for maintaining the level of air as the mixture cures, thus minimizing variability in concrete products.

In various instances, the use of low-NO_x burners in coal-fired boilers has led to either an increase in the amount of unburned carbon in fly ash or large variations in the carbon content of the ash. The variation or increase in carbon content directly impacts the sale of fly ash as a substitute for cement in concrete products because carbon has been observed to impart undesirable properties in the final product. One of those properties is the increase in amount of AEA required, which may be influenced by the amounts and types of carbon forms present.

DISCUSSION

The approach used to characterize the carbon forms in fly ash focuses on controlled-atmosphere programmed-temperature oxidation (CAPTO) partial oxidation followed by characterization of the carbon forms remaining in the fly ash residues. The approach and the CAPTO conditions used were previously described[2].

This oxidative thermal study centers on characterization of the carbon forms present in several fly ash samples produced when a Pittsburgh seam coal was burned in pulverized coal-fired utility boilers equipped with low NO_x burners. The complete CAPTO CO_2 evolution profile of the fly ash carbon was used to establish a temperature regime for progressive partial oxidation studies. A series of samples of fly ash was oxidized, each to a specific temperature, and the residues recovered. The degree of interaction of each residue with surfactant was assessed with an AEA using a previously described foam index (FI) test[2]. An initial decrease in FI was observed upon heating the fly ash to approximately 100°C followed by further decreases in the FI values at higher temperatures as the carbon content diminished.

X-ray photoelectron spectroscopy (XPS) was used to monitor changes in the forms of carbon on fly ash surfaces as a function of temperature during oxidation. Carbon forms were distinguished based on their electrical conductivity under combined irradiation by a monochromatic X-ray source and electron flood gun. By inducing differential charging of the various carbon forms and subsequent processing of the C 1s XPS spectra using factor analysis, three major and one minor forms of carbon were distinguished. The major forms of carbon were assigned to conductive carbon that is not in intimate contact with the ash, insulated carbon that is in intimate contact with the ash, and "adventitious" carbon that is adsorbed on the surface of the fly ash and is a common contaminant detected by XPS on solid surfaces exposed to air.

An attempt was made to correlate differences in carbon forms measured by XPS under increasing oxidation temperature with the resulting decrease in FI values. During oxidation, significant amounts of conductive and insulated carbon were removed from the ash surface, leaving mostly adventitious carbon. Comparison of two untreated fly ash samples from the same utility, and having significantly different FI values, showed that the lower FI was associated with the absence of significant fractions of surface carbon in the conductive and insulated forms, much like the correlation between FI and carbon forms observed following oxidation.

The untreated and partially oxidized fly ash samples were examined by reflected polarized light microscopy. A Zeiss Universal microscope with a 40x oil objective was used for the observations. Photomicrographs of selected fields of view (magnification: 500x) were taken.

Areas of carbon anisotropy were observed in all of the samples except at the oxidized high-end temperatures, where no carbon was observed. Some isotropic areas were observed that contained carbon derived from inertinitic macerals (fusinite, macrinite, etc.), but the majority of the carbon was derived from vitrinite macerals, which occurred as spherical particles and fragments that contained highly porous areas. No evidence was observed for selective oxidation of either anisotropic or isotropic carbon in the fly ash samples oxidized to different temperatures. Iron oxides of various particle sizes and quartz were seen in all samples.

X-ray diffraction analysis of the untreated and oxidized fly ash samples showed decreasing levels of iron oxides (alpha Fe_2O_3 - hematite & gamma Fe_2O_3 - maghemite) with increasing temperature. Two series of samples showed monotonically decreasing levels of iron oxides, while for another series the decrease in iron oxide occurred at a sharper rate beginning at an oxidation temperature of 550°C.

SEM was used to compare the carbonaceous particles in untreated fly ash samples with those in samples oxidized at 550°C in order to determine any morphology changes. Little or no changes in pore structure were noted within the spatial resolution of this technique (~0.1 μm).

REFERENCES

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